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THE PHOTOLYSIS OF CO₂ AT 1849 AND 2139A

by

D. Krezenski, R. Simonaitis and J. Heicklen

October 7, 1971

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The Photolysis of CO_2 at 1849 and 2139 Å

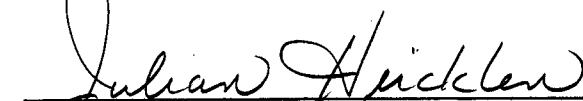
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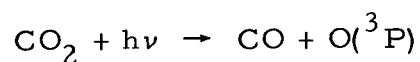
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TABLE OF CONTENTS

Abstract	i
INTRODUCTION	1
EXPERIMENTAL	2
RESULTS	4
ACKNOWLEDGEMENT	6
REFERENCES	7
TABLES	8

ABSTRACT

The quantum yield for the photodissociation of CO_2 at 25°C is 1.08 ± 0.12 for direct photolysis at 1849 Å and CO_2 pressures between 200 and 800 torr; 0.48 ± 0.02 for the Hg $6(^1\text{P}_1)$ sensitized decomposition at CO pressures between 130 and 730 torr; and 0.16 ± 0.05 for the direct photolysis at 2139 Å and CO_2 pressures between 300 and 600 torr. At these wavelengths there is insufficient energy to produce $\text{O}(^1\text{D})$, and the primary process is



INTRODUCTION

The principal atmospheric component of both Mars and Venus is CO₂. Therefore the photochemistry of this molecule is important in the atmospheres of these planets. Previous investigations^{1,2} have shown that the primary photochemical process at 1470 and 1236Å is



and that this process proceeds with unit quantum efficiency. We have now examined the photodissociation of CO₂ at wavelengths with insufficient energy ($\lambda > 1658\text{Å}$) to produce O(¹D) atoms and have found that at 25°C photodissociation occurs. Presumably the primary process is



The quantum yield is 1.08 ± 0.12 for the direct photolysis at 1849Å and CO₂ pressures between 200 and 800 torr; 0.48 ± 0.02 for the Hg 6(¹P₁) sensitized decomposition at CO pressures between 130 and 730 torr; and 0.16 ± 0.05 for the direct photolysis at 2139Å and CO₂ pressures between 300 and 600 torr.

Two studies of the direct photodissociation in this region have been reported recently. DeMore³ found that for CO₂ pressures of 400 psi, the quantum yield of CO production, $\Phi\{\text{CO}\}$, was unity, but Inn⁴ reported $\Phi\{\text{CO}\} = 0.70$ at 29–142 torr of CO₂ for radiation between 1750 and 1850Å. Our results, done at intermediate pressures, support the former measurement. Mori⁵ found that CO was produced in the Hg 6(¹P₁) sensitized photolysis of CO₂ at 1849Å, but quantum yields were not reported.

EXPERIMENTAL

The gases used were Matheson NO, N₂O, and Bone-Dry CO₂. The CO₂ and NO were purified by distillation at -130°C and -186°C, respectively. All three were degassed at -196°C immediately before use.

The reactions were carried out at 25°C in a cylindrical quartz cell 5 cm in diameter and 10 cm long which was connected to a grease free high vacuum line. For the direct irradiations the vacuum line was also Hg free, as ascertained from the lack of product formation from N₂O photolysis at 2537Å. Radiation was from either a Hanovia flat-spiral mercury resonance lamp model No. Z1400-013 (1849A) or a Phillips Zn resonance lamp model No. 93106E (2139A).

For the Hg-sensitized experiments, a drop of mercury was placed in the reaction cell. The Hanovia lamp was enclosed in a cylindrical container and continuously flushed with N₂ to purge O₂, which absorbs radiation at 1849Å. The radiation was also filtered by a LiF window which had been irradiated with a Co-60 source. In this way 2537Å radiation was considerably reduced,⁶ so that N₂O actinometry could be employed.

After photolysis, the gases noncondensable (CO, O₂, N₂) at -196°C were collected and analyzed by gas chromatography utilizing a 1/4-inch diameter column with 5A molecular sieves and a Gow Mac 40-05D power supply in conjunction with thermistor detectors. In the Hg-free system an aliquot was taken, whereas in the Hg-sensitized experiments the whole sample was collected in a Toepler pump.

Actinometry was done with N₂O which photodissociates to give a quantum yield of N₂ formation of 1.41 for all the conditions of this study.⁷ For the direct irradiations, the absorbed intensity, I_a, was

obtained by using pressures of N_2O to exactly match the absorbance at corresponding CO_2 pressures. In this way all geometrical corrections are eliminated. The extinction coefficients used are listed in Table I. Since both absorption spectra are virtually continuous above 1800A, the fact that we used line sources should not introduce errors. For the mercury-sensitized experiments, the absorption of radiation is complete. Actinometer experiments were done with pressures of N_2O equal to those of CO_2 to insure that any pressure-broadening effects would cancel.

RESULTS

The products of the direct photolysis of CO_2 at 1849Å were CO and O_2 . The results are shown in Table II. Experiments were done with CO_2 pressures between 200 and 800 torr for irradiation times of 5 to 784 minutes. The measured values for $\Phi\{\text{CO}\}$ were slightly greater than unity and were invariant to changes in the reaction parameters. The reaction sequence is presumably



The mechanism predicts that $\Phi\{\text{CO}\} = 1.0$ which is nearly obeyed, and that $[\text{CO}]/[\text{O}_2] = 2.0$. The measured values of the ratio $[\text{CO}]/[\text{O}_2]$ are significantly greater than 2.0, thus showing that some of the $\text{O}(^3\text{P})$ atoms are lost at the walls. Such an effect was observed at lower wavelengths in other studies,² as well as in our laboratory in a different system.¹⁰

In an attempt to minimize the wall loss, small amounts of NO were added in a few experiments to aid O_2 production via



These experiments yielded slightly, but not significantly, better results. The average of all the experiments gives $\Phi\{\text{CO}\} = 1.08 \pm 0.12$ and $[\text{CO}]/[\text{O}_2] = 2.25 \pm 0.19$.

In the mercury-sensitized decomposition of CO_2 , again CO and O_2 were produced. However $\Phi\{\text{CO}\}$ dropped markedly as the irradiation time was lengthened, the O_2 deficiency was large ($[\text{CO}]/[\text{O}_2] = 2.6-12$), and HgO was produced. These results agree with those found by Mori,⁵ and can be explained by the fact that $\text{O}(^3\text{P})$ ultimately becomes HgO rather than O_2 . As the HgO accumulates on the cell windows, the absorbed

intensity (and thus the apparent quantum yield) drops. This was confirmed in separate actinometer experiments.

In order to avoid HgO formation, photolyses were done with 0.8-1.0 torr of NO added to produce O₂ via reactions 4 and 5. The resultant quantum yield of CO formation, $\Phi\{\text{CO}\}$ was then independent of irradiation time and CO₂ pressures (130-730 torr). The results are in Table III, and the average value for $\Phi\{\text{CO}\}$ is 0.48 ± 0.02 . Since $\Phi\{\text{CO}\}$ is much less than one, about one half of the Hg 6(¹P₁) quenching by CO₂ is by physical, rather than chemical quenching.

A few runs were done with 2139A radiation. The absorption was very small which necessitated very long runs (~40 hrs.). Thus the results are not too accurate. The average of three experiments between 300 and 600 torr of CO₂ gave $\Phi\{\text{CO}\} = 0.16 \pm 0.05$. Since this value is considerably less than one, deactivation is more important than decomposition. This result is not difficult to understand since radiation at 2139A gives only 6.4 kcal/mole in excess of that needed for dissociation of CO₂. Decomposition from the photoexcited CO₂ molecule is relatively slow, and deactivation can compete effectively.

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TABLE I

Extinction Coefficients

<u>Gas</u>	<u>λ, A</u>	<u>ϵ, cm⁻¹ ^a</u>	<u>References</u>
CO ₂	1849	7.71 x 10 ⁻³	Ogawa ⁸
CO ₂	2139	0.061 x 10 ⁻³	Ogawa ⁸
N ₂ O	1849	3.64	Zelikoff et al. ⁹
N ₂ O	2139	0.090	Zelikoff et al. ⁹

a) Extinction coefficient for a standard atmosphere of gas at 25°C.

TABLE II

Direct Photolysis of CO₂ at 1849Å and 25°C
I_a = 5.3 μ/min.

<u>[CO₂], torr</u>	<u>Irradiation time, min.</u>	<u>Φ{CO}</u>	<u>[CO]/[O₂]</u>
200 ^a	30.0	0.99	1.88
400 ^b	30.0	1.05	1.98
400 ^b	60.0	0.99	2.34
760	5.0	1.38	2.06
790	15.0	1.43	2.35
725	15.0	1.05	2.20
741	30.0	0.97	2.28
700 ^c	30.0	0.92	1.96
775	45.0	1.05	2.50
750	60.0	1.01	2.68
740 ^d	60.0	1.02	2.15
710 ^c	90.0	1.16	2.23
750	91.0	1.14	2.50
800	120.0	1.29	-
690 ^c	180.0	0.99	2.43
790	784.0	<u>0.83</u>	<u>-</u>

ave. = 1.08 ± 0.12

2.25 ± 0.19

a) I_a = 1.36 μ/min.

b) I_a = 2.9 μ/min.

c) 30μ NO also present.

d) 16μ NO also present.

TABLE III

Hg-photosensitized Decomposition of CO₂ at 1849A and 25°C
in the presence of 0.8-1.0 torr of NO.
I_a = 7.35 μ/min.

<u>[CO₂], torr</u>	<u>Irradiation time, min.</u>	<u>Φ{CO}</u>
130	15.00	0.46
213	15.00	0.47
401	15.00	0.46
410	10.00	0.51
420	2.00	0.50
730	15.00	<u>0.51</u>

ave. = 0.48 ± 0.02